

FARADAY'S RESEARCHES IN ELECTRO-CHEMISTRY

By ARTHUR MARSHALL

It was through electrochemistry that Faraday became a scientist or "natural philosopher" as he described himself. For in 1812, when he was a journeyman bookbinder, 21 years of age, he attended a course of lectures by Sir Humphry Davy at the Royal Institution on this subject. He made notes of the lectures, wrote them up, bound the volume neatly, and submitted it to Davy with the request that he might be found scientific employment. This led to his being employed in the following year as assistant in the laboratory at 25 shillings a week.

His first important paper on electrochemistry was published in 1832, when he had already made his great discovery of the production of electricity from magnetism. It constituted the third series of his *Experimental Researches in Electricity* and dealt with the identity of electricities from different sources, clearing up finally a question which had puzzled the greatest scientists of the time. Five different sources of electricity were dealt with, namely, voltaic, ordinary, magneto-, thermo-, and animal. Voltaic electricity was that obtained from the voltaic pile or cell; ordinary was that with which the scientific world had longest been familiar; the electricity obtained from the influence machine; magneto-electricity was that which he had himself discovered in 1831; thermo-electricity the current obtained from a heated thermocouple; and animal electricity the shocks produced by certain aquatic animals, such as the gymnotus (electric eel) and torpedo. That there had until then been a real doubt as to these identities is shown by the fact that in the very last paper published by Sir Humphry Davy in November, 1828, he arrived at the conclusion that "animal electricity was distinctive and peculiar."

Eight different tests were applied to establish these identities, namely, physiological effects, magnetic deflection, magnets made, spark, heating power, true chemical action, attraction and repulsion, discharge by hot air. So that forty separate trials were necessary for the complete investigation, and all of these except five were actually carried out, these five being prevented only by the primitive state of the technique available. The results left no doubt as to the identities of all the electricities.

The second part of this communication deals with the relation by measure of common and voltaic electricity, and, although short, is even more important than the first part, for it contains the statement of Faraday's First Law of Electrolysis. Faraday used two distinct measures of the "absolute quantity of electricity": (a) the swing imparted to the needle of a galvanometer and (b) the amount of chemical change effected as shown by the depth or tint imparted to potassium iodide paper by a platinum wire pressing on it, the paper being supported on a platinum spatula. With such simple appliances did he make these important discoveries! He found that the two measures were proportional to one another in all circumstances, whether common or voltaic electricity were used. In this

research Faraday already distinguished clearly between tension or intensity and quantity of electricity, or, as we should now say, between potential difference and current, or volts and amperes. His first statement of the Law was "chemical power, like magnetic force, is in direct proportion to the absolute quantity of electricity which passes."

The fourth, fifth, and seventh series of *Experimental Researches in Electricity*, published in the following year, 1833, also deal with electrochemistry. The fourth series is about the conducting power of various substances in the solid and liquid states. Faraday discovered that when water is frozen its conductivity is almost destroyed. Extending his investigation, he found that a large number of salts, oxides, and sulphides behaved similarly, their conductivity when molten being considerable, and accompanied by electrolytic decomposition. This was an important discovery, as it had previously been supposed by Davy and others that such decomposition could only be effected in the presence of water, in spite of some facts already known which were not in agreement with this supposition.

In the fifth series he dealt further with these matters, and discussed what happens in an electrolyte when a current passes through it. As the result of various experiments, he came to the conclusion that chemical changes are not confined to the places where the metal wires or plates dip into the substance undergoing change, but are taking place along the whole course of the current. He gave a simple diagram showing how the substance becomes split up into two sorts of particles which travel in opposite directions.

This series also contains the first statement of Faraday's Second Law of Electrolysis: "For a given quantity of electricity, whatever the decomposing conductor may be, whether water, saline solutions, acids, fused bodies, etc. the amount of electrochemical action is also a constant quantity, i.e., would always be equivalent to a standard chemical effect founded upon ordinary chemical affinity." These are only a few of the matters dealt with.

The two Laws may be combined as follows: "If a current passes through an electrolyte, bringing about changes at the electrodes, the quantity of each substance formed will be directly proportional to its equivalent weight, to the strength of the current, and to the time of passage of the current." (Allmand and Ellingham, *Principles of Applied Electrochemistry*, 2nd ed., p. 15.)

In the seventh series he started by introducing the following new words, without which he had found great difficulty in expressing his results:

Electrode, anode, cathode,
Electrolyte, electrolyse, electrolytical,
Ion, anion, cation.

These terms, with derivatives of them, such as anolyte and catholyte, have been adopted universally and have proved indispensable. Faraday applied the terms ion, anion, and cation to the constituents, or radicals, in bulk, but later they came to be used for the individual particles.

He then proceeded to establish his Second Law experimentally by the electrolysis of fused electrolyte, and he ascertained what substances conduct electrolytically and what do not.

Faraday introduced a new "Measurer of Volta-electricity," which he called a "volta-electrometer," depending on the measurement of the volumes of hydrogen and oxygen evolved when the current was passed through dilute sulphuric acid. He described various modifications of this instrument, now generally called a voltmeter or coulommeter, and discussed sources of error in its use. He also dealt with the difficult question of what are the primary products of electrolysis and what secondary. It was to avoid complications arising from secondary effects that he carried out numerous experiments with fused anhydrous salts, such as the chlorides of silver and lead. Incidentally he introduced the use of graphite (plumbago) electrodes.

He found that when an amalgamated zinc plate was immersed in dilute sulphuric acid and connected by a wire with a platinum plate dipping into the same vessel, the hydrogen evolved at the latter was equivalent to the zinc dissolved, and therefore to the electricity conveyed by the connecting wire. This was a further confirmation of the Second Law, but he was at the time doubtful about explaining these phenomena by the adoption of Dalton's atomic hypothesis.

The eighth, sixteenth, and seventeenth series of the Experimental Researches in Electricity are devoted to the theory of the voltaic pile or battery, and demonstrate that its action is due to chemical reactions and not to mere contact of dissimilar metals, or of the electrodes with the electrolyte, as was maintained by Volta and many of the foremost investigators of the day, especially in Italy and Germany. This controversy has long ceased, and we do not find it, or most of the experiments by which Faraday established his case, so interesting as the work with which we have already dealt, but they rendered clearer and ever more clear the conceptions he had laid down.

In the eighth series, published in 1834, he showed first of all that a battery cell would work when there was no direct contact between dissimilar metals, and he also investigated the polarisation of the cells.

As this paper did not convince the advocates of the contact theory, he returned to the subject in the sixteenth and seventeenth series, published in 1839, and rendered this theory quite untenable. Incidentally he worked out a series of metals and other substances that can be used as electrodes in the order of their potential differences, and showed that they are different in different electrolytes. He also discovered that iron which has been cleaned thoroughly becomes covered at once with an invisible film of oxide, a fact which was rediscovered by Haber in 1906. Tyndall in his book on "Faraday as a Discoverer" says of this communication: "In this paper he hampered his antagonists with a crowd of adverse experiments. He hung difficulty after difficulty about the neck of the contact theory,

until in its efforts to escape from his assaults it so changed its character as to become a thing totally different from the theory proposed by Volta. The more persistently it was defended, however, the more clearly did it show itself to be a congeries of devices, bearing the stamp of dialectic skill rather than of natural truth."

In conclusion Faraday pointed out that the contact theory would involve a *creation of power*, and be like no other force in nature. "Then would the perpetual motion also be true," he said. This was a remarkable pronouncement, as it was made more than two years before either Mayer printed his brief but celebrated essay on the Forces of Inorganic Nature, or Joule published his first famous experiments on the Mechanical Value of Heat. But Faraday had himself been anticipated by Dr. Roget in 1829, as he admitted in a note added to his memoir. Tyndall concludes: "When this argument had clearly fixed itself in his mind, Faraday never cared to experiment further on the source of electricity in the voltaic pile. The argument appeared to him to remove the *foundation itself* of the contact theory, and he afterwards let it crumble down in peace."

FARADAY'S VIEWS ON PASSIVITY IN THE LIGHT OF RECENT RESEARCH

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The chemical inertness of iron which has been immersed in concentrated nitric acid was observed by Keir¹ in 1790, and Faraday's attention was directed to the phenomenon by a letter received from Schönbein, dated May 17, 1836. A month later, Faraday² sent a communication to the *Philosophical Magazine* in which was set forth an explanation of the "peculiar state" of iron. This explanation appears to have been influenced by Schönbein's observation that iron was made indifferent to nitric acid of sp. gr. 1.35 either by oxidising the metal by heating in air or by previous immersion in more concentrated nitric acid, suggesting that concentrated nitric acid has some oxidising action on the metal.

Faraday writes: "My strong impression is that the surface of the iron is oxidised, or that the superficial particles of the metal are in such relation to the oxygen of the electrolyte as to be equivalent to an oxidation; and that having thus their affinity for oxygen satisfied, and not being dissolved by the acid under the circumstances, there is no renewal of the metallic surface, no reiteration of the attraction of successive particles of the iron on the elements of successive portions of the electrolyte, and therefore not those successive chemical actions by which the electric current (which is definite in its production as well as in its action) can be continued."

A foundation for the protective oxide-film theory of passivity was thus laid almost a hundred years ago, but the theory did not gain general acceptance until recent times, and meanwhile the view gained ground that the metal is transformed into an inert, allotropic modification when it becomes passive. Such views were expressed by Berzelius in 1844, by Hittorf in 1898, and in more recent times the